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# Optical characterization of directly deposited graphene on a dielectric substrate

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**Abstract:** By using scanning multiphoton microscopy we compare the nonlinear optical properties of the directly deposited and transferred to the dielectric substrate graphene. The direct deposition of graphene on oxidized silicon wafer was done by utilizing sacrificial copper catalyst film. We demonstrate that the directly deposited graphene and bi-layered transferred graphene produce comparable third harmonic signals and have almost the same damage thresholds. Therefore, we believe directly deposited graphene is suitable for the use of e.g. nanofabricated optical setups.

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## 1. Introduction

Scalable and position-controlled synthesis of graphene remains a major obstacle preventing the incorporation of graphene elements into electronic and optoelectronic devices [1]. In the search for reliable techniques, the attention of the carbon community is mainly concentrated on the chemical vapor deposition (CVD), which is widely recognized as a promising technique to produce large area graphene sheets of high crystallinity [2,3]. However, the major disadvantage of the CVD technique is that it allows one to synthesize graphene only on the surface of a transition metal substrate [3]. In order to incorporate graphene into electronic and optoelectronic devices, this technique should be complemented with the transferring of a one atom thick film into a dielectric or semiconductor environment. This transfer process inevitably increases the number of defects in graphene which results in deterioration of its electronic properties and radically increases the material cost [3]. Correspondingly, scalable and controllable synthesis of graphene on dielectric and semiconductor surfaces is one of the most eagerly waiting breakthroughs in carbon research [1].

Among large number of papers devoted to a direct graphene synthesis on dielectric substrates, the CVD based technique that utilizes sacrificial pre-deposited copper nanolayer deposited on a dielectric substrate is of special interest [4–6]. In this technique, the pre-deposited thin copper layer ensures catalytic synthesis of graphene on its surface. However, since the thickness of the copper film is small, the sheet of highly crystalline graphene grows on both top (i.e. copper/atmosphere) and bottom (copper/substrate) interfaces [5,6]. Thus, by removing the copper film (along with the top graphene), one arrives at a few-layer graphene deposited on the dielectric substrate.

Although the above technique opens avenues towards position-controlled and scalable deposition of graphene on a dielectric substrate, it suffers from two serious flaws. These are (i) fluctuating thickness and (ii) reduced electron mobility of the deposited graphene [5,6]. Overcoming these difficulties will allow the employment of the direct deposition technique for fabrication of the graphene-based electronic devices.

In this paper, we report a comparative study on the graphene fabricated by conventional transfer method and graphene grown directly on a dielectric substrate using nonlinear optical microscopy. We also characterized the transferred and directly grown graphene samples by scanning electron microscopy (SEM), spectrophotometry and Raman spectroscopy.

## 2. Sample preparation

The reference graphene sample was grown on a copper foil (25  $\mu\text{m}$  thick, 99.8% pure) by using conventional hot wall CVD. Following standard procedure [3,7], the Cu foil was first heated up to 1000  $^{\circ}\text{C}$  and annealed for 30 min in hydrogen flow (5 sccm, 0.1 mbar). Annealing followed by 15 min graphitization using hydrogen-methane gas mix (5 sccm: 5 sccm flow rates with 0.2 mbar pressure). Multilayered graphene areas, grown by template graphene growth, were removed by brief hydrogen etching right after graphitization [8]. Graphene was transferred from Cu foil to the Si/SiO<sub>2</sub> (300 nm) by PMMA based technique described in more detail in [9], by Li et al..

In order to synthesize graphene directly on dielectric, the Si/SiO<sub>2</sub> (300 nm) substrate was coated with  $\sim$ 250 nm thick copper layer by using physical vapor deposition (PVD). After the copper deposition, the sample was processed in the CVD chamber. The direct deposition process used here was slightly different compared to the graphene deposition on a foil [6]. At

first the sample was heated up to 700 °C in H<sub>2</sub> flow (5 sccm). At 700 °C H<sub>2</sub> + CH<sub>4</sub> gas mix (1:1) was injected in the chamber and the chamber was heated up to 950 °C with 10 °C/min heating rate in a static atmosphere (~5 mbar). It is worth noting that in order to avoid evaporation and/or dewetting of the copper film deposited on dielectric substrate we shorten the CVD process time and slightly decrease the maximum temperature in comparison to those used in the graphene synthesis on the copper foil. The 950 °C temperature was kept for 5 min and the chamber was then cooled down to 700 °C in one and a half hours. The rest of the cooling was done in H<sub>2</sub> atmosphere (5 mbar). After the CVD process the top layer graphene on the Cu film was removed by oxygen plasma. The graphene grown to the interface of copper and Si/SiO<sub>2</sub> was protected by the copper layer, which was mostly continuous although dewetting did produce randomly distributed small holes. This Cu layer was removed by iron(III) chloride wet etching.

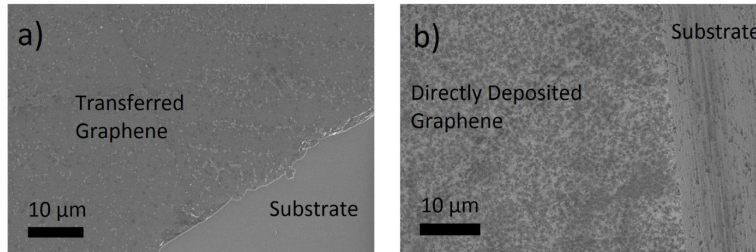


Fig. 1. (a) SEM images of transferred, monolayer graphene on Si/SiO<sub>2</sub> substrate. On top of the graphene, one may observe small droplets of PMMA remains that originate from the transfer process. (b) Directly deposited graphene on Si/SiO<sub>2</sub> substrate. Although the material seems rather grainy, it is continuous throughout the substrate (see also [5,6]).

### 3. Experimental methods

Figure 1 shows typical SEM images of transferred and directly grown graphene sample surfaces. It is noteworthy that the transferred graphene is rather uniform, while in the directly deposited graphene sample, the number of deposited graphene layers fluctuates from point to point. Strong electron scattering, caused by such a grainy structure is probably the main reason for the relatively low electron mobility (~300 cm<sup>2</sup>/Vs) of the directly grown graphene [5]. However, surprisingly the reflectance spectra (Fig. 2) of the transferred graphene and the directly deposited graphene are very similar indicating similar absorption properties of both samples. In order to visualize the difference in optical properties between transferred and directly grown graphene we employed nonlinear microscopy technique.

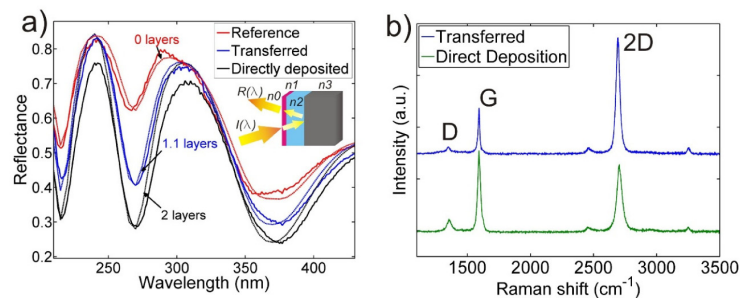


Fig. 2. Linear optical characterization of transferred and directly grown graphene. (a) Number of graphene layers can be estimated on Si/SiO<sub>2</sub> substrate by absorption. For transferred graphene the average graphene film thickness is 1.1 layers, thus 90% of the material is monolayer consisting of a few areas with bi-layers. Directly deposited graphene has the average absorption of 2 graphene layers. (Fitting was done according [10] and [11]) (b) Typical Raman spectrum of the transferred graphene shows very typical features of monolayer graphene, while the broadened 2D peak in the directly deposited graphene indicates the presence of a few-layer graphene. The excitation wavelength in Raman measurements was 514 nm.

We used a multiphoton femtosecond microscope [12–14] introduced schematically in Fig. 3. In brief, the linearly polarized excitation light from a fiber laser operating at 1560 nm with 150 fs pulse length and 8 MHz repetition rate, is focused on the sample's surface through a 20x microscope objective (New Focus 5724 H-C, 0.5NA) creating a laser spot with diameter of 1.8  $\mu\text{m}$ . The backscattered second harmonic generation (SHG) and third harmonic generation (THG) light are collected by the same objective lens and split by a dichroic mirror, which divides photons from the SHG and THG signals to two separate photomultipliers. Additional band-pass filters with central wavelengths of 525/35 nm and 780/12 nm allow only the THG and SHG to reach the photomultipliers, respectively.

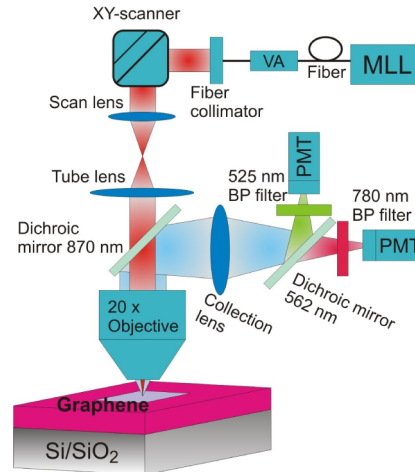


Fig. 3. Schematic diagram of the multiphoton microscope. The mode-locked femtosecond fiber laser beam is guided from the source (MLL) to the sample surface through a dichroic mirror and focused with a 20x objective lens. The backscattered second (780 nm) and third (525 nm) harmonic signals are filtered before the photomultiplier tubes (PMTs).

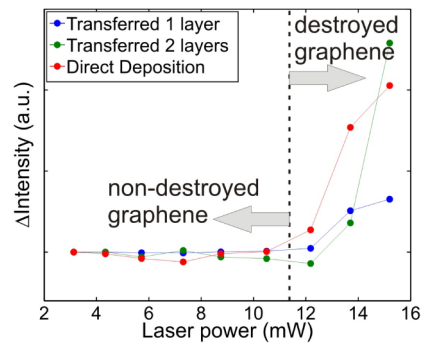


Fig. 4. Damage threshold of directly deposited graphene is comparable to mono- and bi-layered graphene prepared by the transfer technique.  $\Delta\text{Intensity}$  is the intensity difference of THG signal between the studied area and the reference area. The damage area has less THG than the pristine area.

#### 4. Results and discussion

In order to evaluate the damage threshold of the graphene samples, we irradiated the samples with femtosecond laser pulses. Since the light-induced breaking of the carbon bonding leads to decrease of the THG signal (see also [15], by Roberts et al.), the damage (ablation) threshold can be visualized by measuring dependence of the THG signal on the fundamental beam power. Specifically, we compared the intensity of the THG signal obtained from the

areas pre-exposed with an intense fundamental beam to the intensity of the THG signal from the unexposed area. One can observe from Fig. 4 that both transferred and directly grown graphene have the same damage threshold. To avoid destroying samples in the multiphoton microscopic measurements, the fundamental beam power did not exceed the damage threshold of graphene of 11.2 mW (see Fig. 4). This power corresponds to the peak intensity of about  $360 \text{ GWcm}^{-2}$ .

To measure the THG signal from a few graphene layers, we irradiated areas with a folded graphene sheet in the transferred graphene sample. One can observe from Fig. 5 (a) that one, two and four-layer graphene can be clearly distinguished.

To be able to compare THG signals directly, the directly deposited graphene was studied with the same laser power and photomultiplier tube amplifications as the transferred graphene. As it can be seen in Fig. 5(b) the directly deposited graphene gives a signal comparable with that of the transferred CVD graphene. However, the third harmonic image of the monolayer CVD graphene is rather uniform, while the scanned image of the directly deposited graphene is not as uniform on the micrometer scale. By comparing the THG signal intensity from both samples, one may conclude that the directly deposited graphene consist of one, two and three layer thick graphene grains. This result is in perfect agreement with the linear optical measurement, shown above, where the average layer thickness was estimated to 2 layers.

In the experiment, we observed the nearly equal damage threshold for the transferred and the directly grown graphene. Moreover, the obtained damage threshold in both samples is about the same,  $360 \text{ GWcm}^{-2}$ , which is in the range of previously reported values from  $300 \text{ GWcm}^{-2}$  to  $3 \text{ TWcm}^{-2}$  [15,16]. This finding is rather surprising because the directly grown graphene is much more grainier in comparison with the transferred graphene. However, when the carbon structure becomes very amorphous (e.g. pyrolytic carbon), the damage threshold will be reduced a few orders of magnitude [17]. The phonons, which are the major heat carriers, should scatter on the grain boundaries and hence the directly grown graphene should be damaged at lower beam power than transferred graphene.

This result was unexpected and may originate from the PMMA remains on top of the transferred graphene (see Fig. 1). Under high laser exposure these polymer remains may act as heating centers, which can damage the transferred graphene under laser irradiation. Another possible reason is the good graphene flake interconnection in the directly deposited graphene. The grain size of directly grown graphene was estimated to be about micron scale, while for transferred graphene the grain size is order of tens of microns. Despite the grains are very small in the directly deposited graphene the interconnection can be good enough for heat dissipation.

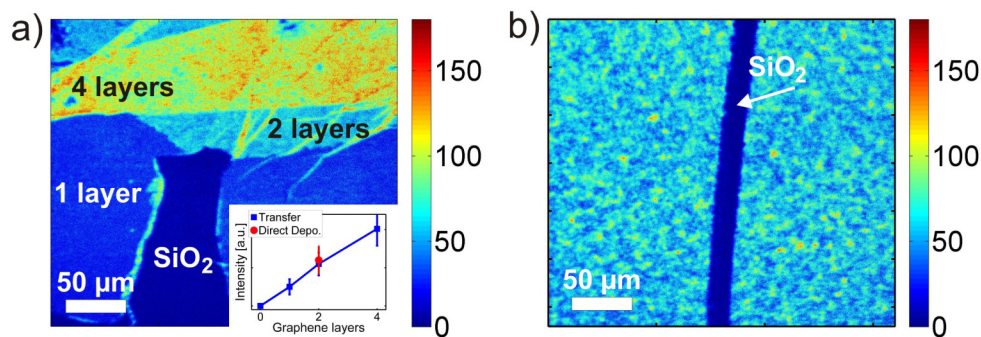


Fig. 5. Multiphoton microscopic images of (a) transferred graphene film with a tear and folded areas and (b) directly deposited graphene with a scratch made by a scalpel. (a-inset) average graphene film thickness is comparable to folded bi-layered graphene prepared by transfer technique. (Both image size is about  $300 \times 300 \mu\text{m}^2 \mu\text{m}$ . Color bar indicates the intensity of THG signal.)

Since the direct deposition technique relies on a pre-deposited copper film, the space-selective deposition of graphene can be achieved by using conventional lithography techniques. However, it is worth mentioning that at elevated temperature, the melting of the copper film may complicate the nanofabrication of the directly grown graphene. Nevertheless, these complications can be easily avoided by post patterning the Cu film after the CVD process. Thus, the proposed fabrication technique allows very precise localization and even self-assembling graphene growth [18,19].

Because the nonlinear THG signal was comparable to that of conventionally grown CVD graphene, we believe that the direct deposition technique could provide very efficient platform for optical use of directly grown graphene. More specifically, directly grown graphene could be working as a saturable absorber in lasers, nonlinear optical material for plane-waveguide optics or after patterning be an optical metamaterial. Therefore, directly deposition technique can be a very powerful tool for integrating graphene on nanofabricated optical setups.

## 5. Conclusion

In conclusion, we characterized the damage threshold and nonlinear optical third harmonic generation from directly deposited graphene. Although the electron mobility in transferred graphene is demonstrated to be much higher in comparison to directly grown graphene, the optical properties seem to be similar. Therefore, we believe that directly deposited graphene is a potential material in the field of photonics applications

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